CRYSTALLIZATION BEHAVIOUR OF HYDROGENATED RAPESEED OIL

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Low erucic acid rapeseed oil from Brassica napus (Zephyr) was hydrogenated under selective conditions (205°C, 0.02% nickel) and non-selective conditions (107°C, 0.04% nickel). Seven samples of different iodine value in each series were obtained and analyzed for fatty acid composition, iodine value and trans isomer content. The changes in 18 carbon fatty acids with the progress of hydrogenation are presented in Figure 1. There was little difference in the pattern of change. For samples with iodine values greater than 75, selective hydrogenation produced more of the 18:1 acids and less of the 18:0 fatty acids. The pattern was reversed in samples with iodine values of less than 75. The major difference between the selective and non-selective series was in the trans isomer content. Within each series, trans content increased to a maximum and then declined as hydrogenation progressed. At any given iodine value the selectively hydrogenated oil contained a higher level of trans isomers as shown in Figure 2.

Solid fat indices of the two series of hydrogenated oil are presented in Figure 3. Selectively hydrogenated samples had steeper melting curves than non-selectively hydrogenated samples. At the same iodine value a selectively hydrogenated oil was much harder than a non-selectively hydrogenated oil. This was also evident from the dropping points of the oils as shown in Figure 4. Ordinarily, in the hydrogenation of oils greater selectivity produces less saturation and, therefore, softer fats. In this case selectivity resulted in harder fat because of the higher trans content.

Polymorphic stability of the three harder samples of each series of hydrogenated oils was measured by infra red spectrophotometry. No difference in stability was detected between samples from the same series, but there was a marked difference between series. The selectively hydrogenated samples exhibited beta crystals after 9 hours, the non-selectively hydrogenated samples only after 48 hours. Similar results were obtained by X-ray diffraction analysis.

Changes in the size of fat crystals were observed with polarized light microscopy. All samples showed increased crystal size with time as shown in Figure 5. The rate of crystal growth was temperature dependent, higher growth rates were observed at higher temperatures. As indicated in Figure 6 the selectively hydrogenated samples developed larger crystals than non-selectively hydrogenated samples under the same conditions of temperature and time. At the same temperature, crystal size was dependent on iodine as shown in Figure 7. Samples of oil of higher value were observed to develop larger crystals. This was true for selectively as well as non-selectively hydrogenated samples.

Two- and three-component margarine blends were prepared from the hydrogenated oil samples. These oil blends were prepared to have an SFI value of 14-21 at 20°C and a dropping point in the range of 32-35°C. Three sets of blends were selected to investigate separately the effect of trans content, iodine value and blend composition on polymorphic stability. Set A consisted of blends of approximately equal iodine value but widely

different trans content. Set B consisted of two groups of three blends each with approximately equal amounts of trans isomers but differing in iodine value. Set C consisted of four blends differing in hard fraction component, two containing non-selective hard fractions and two containing selective hard fractions. Polymorphic stability of these blends was determined with the infra red method. Results obtained with set A (table 1*) show that for each pair of blends of equal iodine value the one with the higher trans content underwent transition to the beta form faster, and therefore was considered less stable. Results for set B indicate that for each group containing equal amounts of trans isomers stability decreased with increasing iodine value. The results of set C were more difficult to interpret. It appeared that blends containing selectively hydrogenated harder component were less stable than those containing non-selectively hydrogenated harder component. However, in this set the effect of trans content, type of harder component and iodine value are difficult to separate.

It was observed that solid fat content as determined by wide-line NMR increased during storage for several days. It was assumed that this was a manifestation of polymorphic instability. The relationship between solid fat content and storage time for the three sets of margarine oil blends is presented in Figures 8, 9 and 10. If the time taken for reaching a constant solid fat content was considered as a measure of polymorphic stability there was good agreement between these results and the measurements reported in Table 1 obtained by the infra red method. The faster a plateau is reached the less stable the fat is judged to be. A control fat consisting of a commercial margarine oil without inclusion of rapeseed oil appeared quite stable under the conditions of these tests.

Examination of the margarine blends by polarized light microscopy after holding at 20°C demonstrated the existence of large crystals in all blends by the second day of storage. Photomicrographs of crystals in three of these blends are presented in Figure 11. Although this method is of a qualitative nature, it does readily indicate the changes that take place in the crystal structure of these fats.

Five of the margarine oil blends were selected for preparation of margarine in a pilot scale unit (Bullock, et al., 1971). These margarines were evaluated for crystal size and consistency as a function of time and temperature of storage. The solid fat content, dropping point, iodine value and trans content of these margarine blends are presented in Table 2. When these margarines were kept at 20°C for up to four weeks there was a distinct difference in crystal size as is demonstrated by Figure 12. The non-selective blend E had a much smaller crystal size pattern than the others. When these margarines were subjected to repeated temperature cycling (storage for 4 days at 5°C followed by 3 days at 20°C), all of the five margarines developed large crystals as shown in Figure 13. Measurement of the consistency of these margarines when kept at 20°C indicated that some of the samples became harder during storage as shown in Figure 14. Consistency of the margarines subjected to cycling temperature treatment resulted in considerable hardness increase for all but one of the samples (Figure 15).

There have been a few reports in the literature suggesting the possibility of varying the chemical and structural characteristics of hydrogenated fats to bring about changes in the polymorphic behaviour (Hoerr and Ziemba, 1965; Merker et al., 1958). The work reported in this paper indicates that the physical properties of low erucic acid rapeseed oil

*The tables are not included by the author

hydrogenated under different conditions may show considerable variation. Although the non-selectively hydrogenated fats were more stable the improvement was not sufficient to prevent formation of large crystals and graininess under most conditions of storage. However, this work provides a basis for further attempts to improve the physical properties of margarines made from rapeseed oil.

REFERENCES

Bullock, D.H., K.C. Thomas and L.M. McKnight, 1971. Commercial production of low-fat dairy spread made possible by new method. Modern Dairy, September, 14-15.

Chapman, D., 1965. The structure of lipids by spectroscopic and x-ray techniques. Methuen and Co., London

Hoerr, C.W. and J.V. Ziemba, 1965. Fat crystallography points the way to quality. Food Eng. 37 (5), 90.

Merker, D.R., L.C. Brown and L.H. Wiedermann, 1958. Relationship of polymorphism to the texture of margarine containing soybean and cottonseed oil. J.Am.Oil Chemists' Soc., 35, 130.

Mertens, W.G. and J.M. deMan, 1972b. The influence of temperature treatment on solid-liquid ratios of fats determined by wide-line nuclear magnetic resonance. Can.Inst. Food Sci. Technol. J., 5, 77.

Shehata, A.A.Y. and J.M. deMan, 1970. A sample and rapid method for the preparation of methyl esters of fats in milligram amounts for gas chromatography. Can.Inst.Food Sci.Technol.J., 3, 85.

Weinberg, B., 1972. Processing of low erucic rapeseed and of canbra oil. Can.Inst.Food Sci.Technol.J., 5, A57.

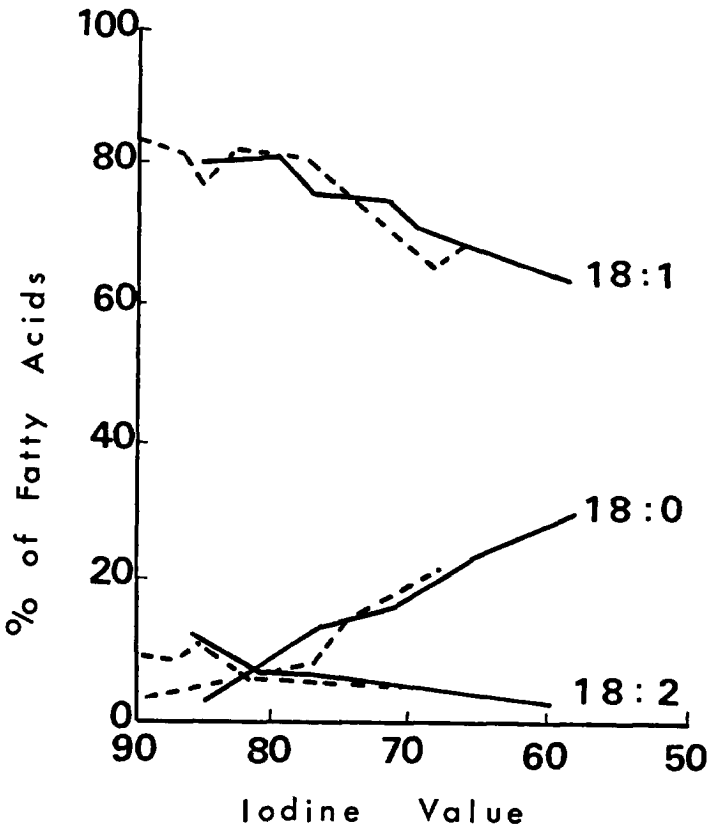

FIG. 1

DISTRIBUTION OF 18 CARBON ATOM FATTY ACIDS IN HYDROGENATED RAPESEED OIL AS A FUNCTION OF IODINE VALUE. (SOLID LINES - NON-SELECTIVE HYDROGENATION, DOTTED LINES - SELECTIVE HYDROGENATION).

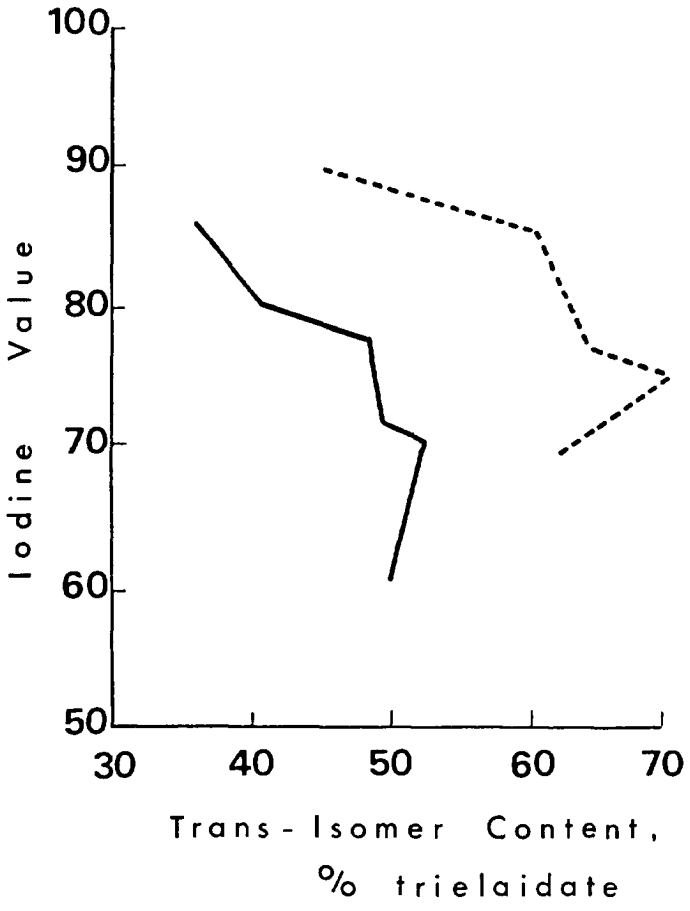

FIG. 2

TRANS ISOMER CONTENT OF HYDROGENATED RAPESEED OIL. (SOLID LINE - NON-SELECTIVE HYDROGENATION, DOTTED LINE - SELECTIVE HYDROGENATION).

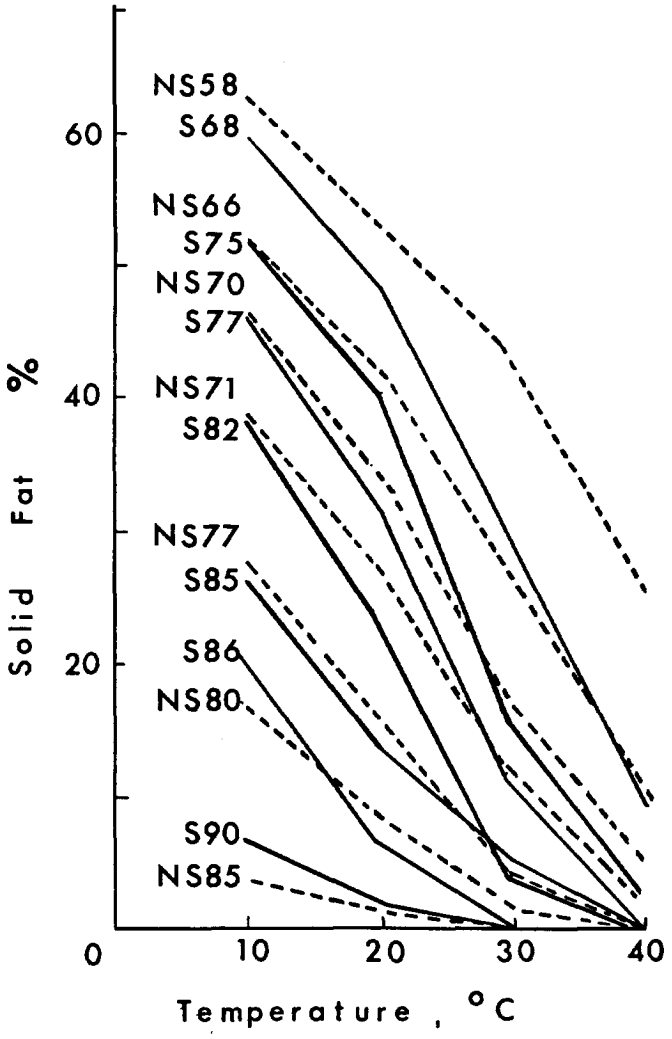

FIG. 3

SOLID FAT CONTENT OF HYDROGENATED RAPESEED OIL. (SOLID LINES - SELECTIVE HYDROGENATION, DOTTED LINES - NON-SELECTIVE HYDROGENATION).

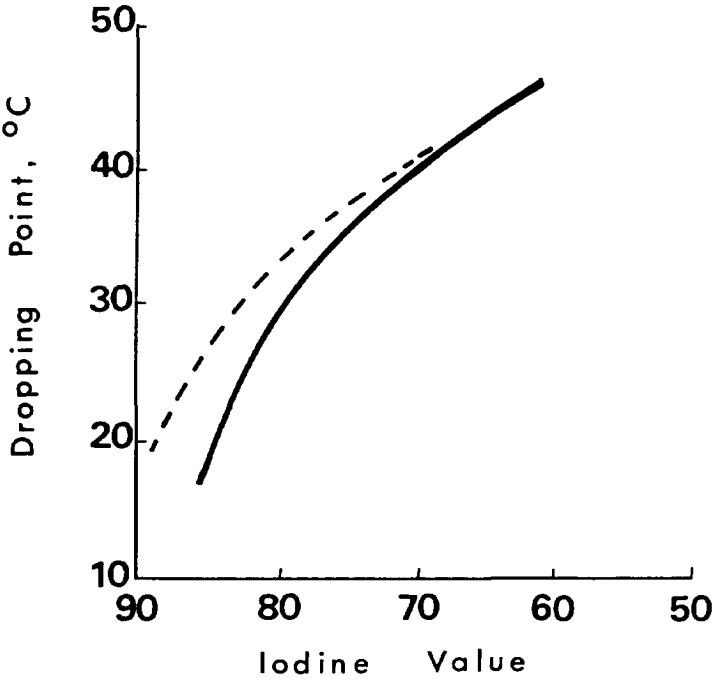

FIG. 4

DROPPING POINT OF HYDROGENATED RAPESEED OIL. (SOLID LINE - NON-SELECTIVE HYDROGENATION, DOTTED LINE - SELECTIVE HYDROGENATION).

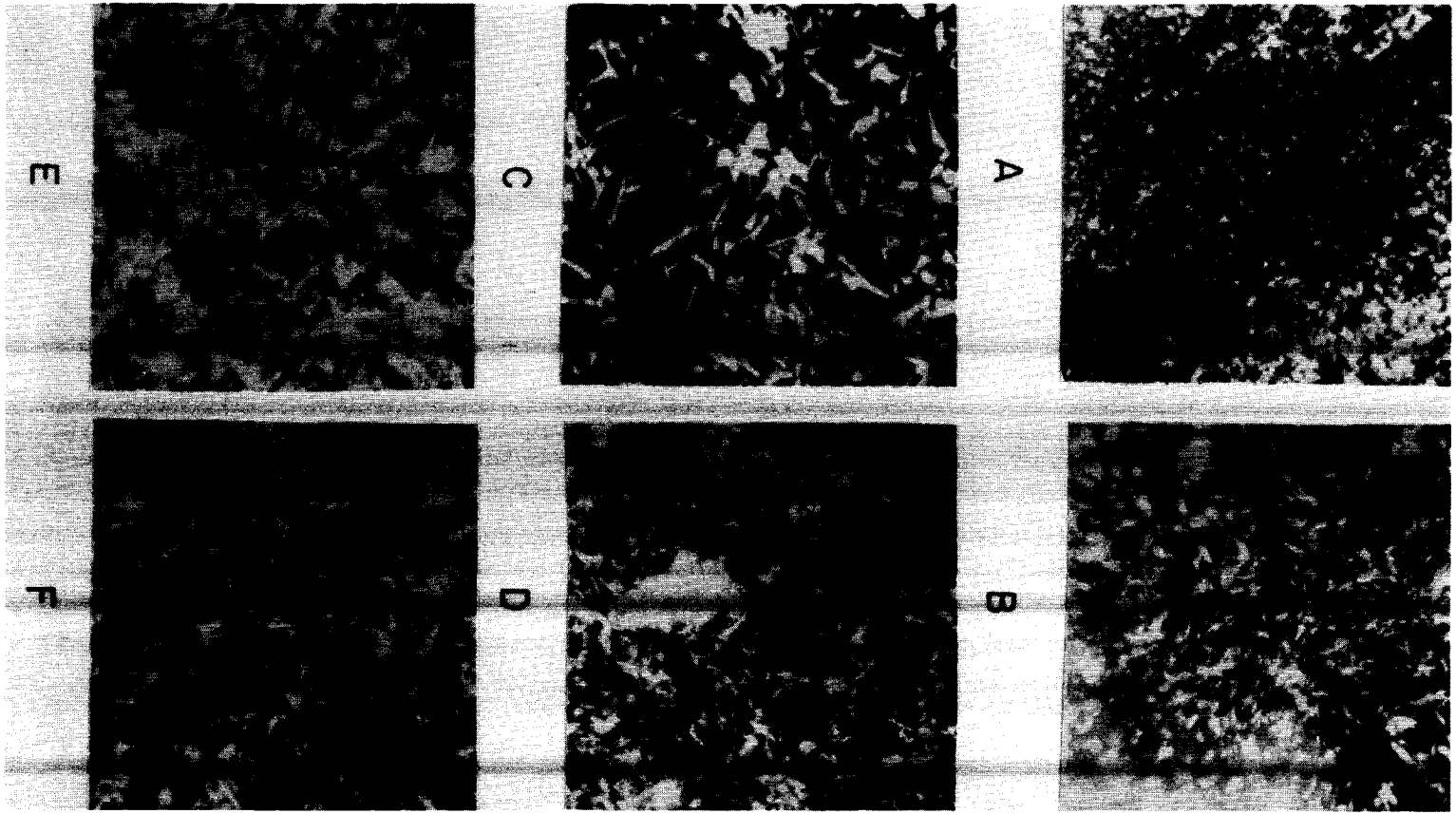

FIG. 5

EFFECT OF TIME AND TEMPERATURE ON CRYSTAL GROWTH OF HYDROGENATED RAPESEED OIL. A, B, C SAMPLE KEPT AT 32°C FOR 2, 5 AND 24 HOURS, RESPECTIVELY. D, E, F SAMPLE KEPT AT 37°C FOR 2, 5 AND 24 HOURS, RESPECTIVELY.

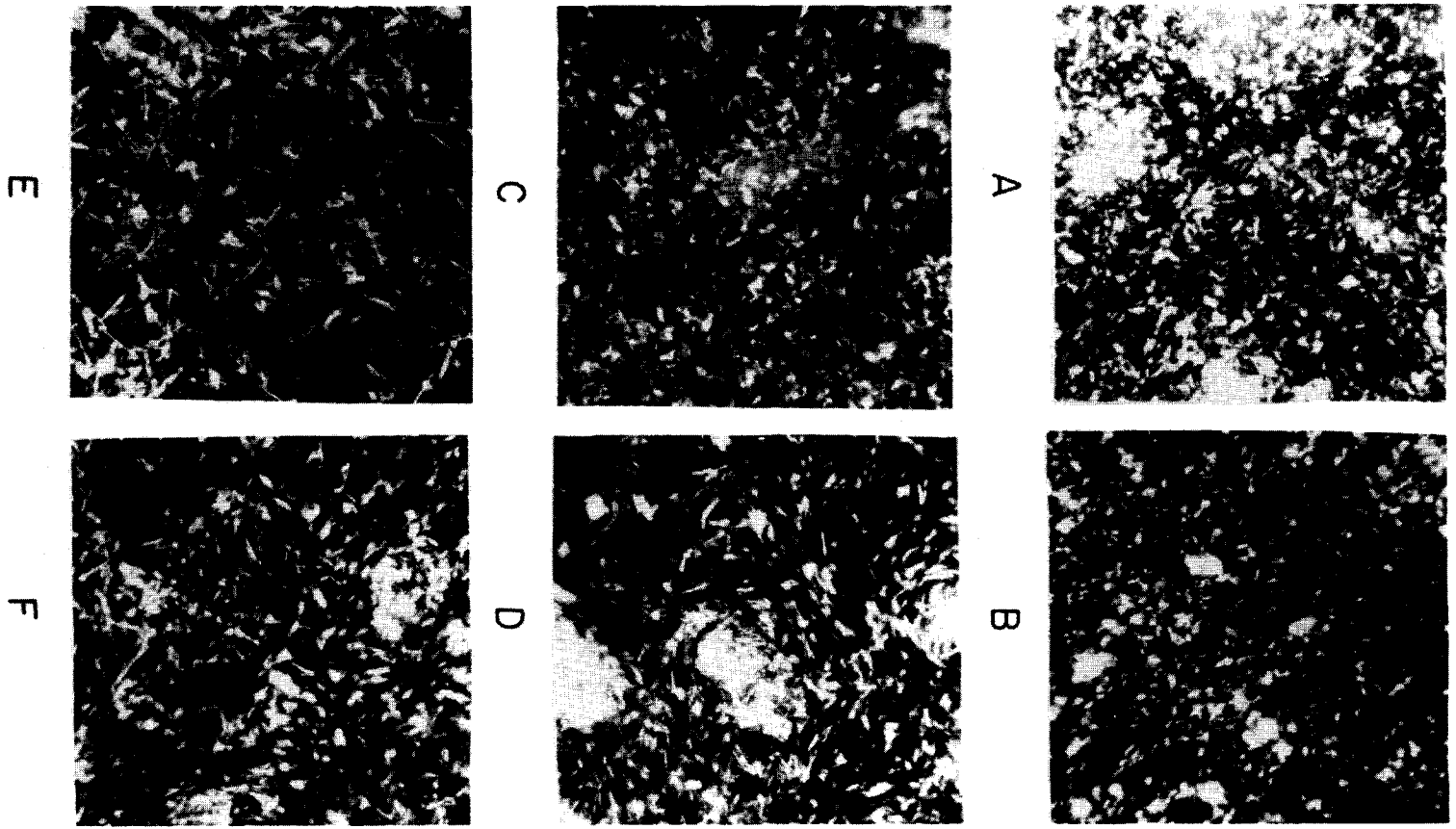

FIG. 6

EFFECT OF HYDROGENATION CONDITIONS ON CRYSTAL GROWTH IN HYDROGENATED RAPESEED OIL. SAMPLES KEPT AT 32°C FOR 24 HOURS. A - SAMPLE NS58; B - SAMPLE NS66; C - SAMPLE NS70; D - SAMPLE S68; E - SAMPLE S75; F - SAMPLE S77.

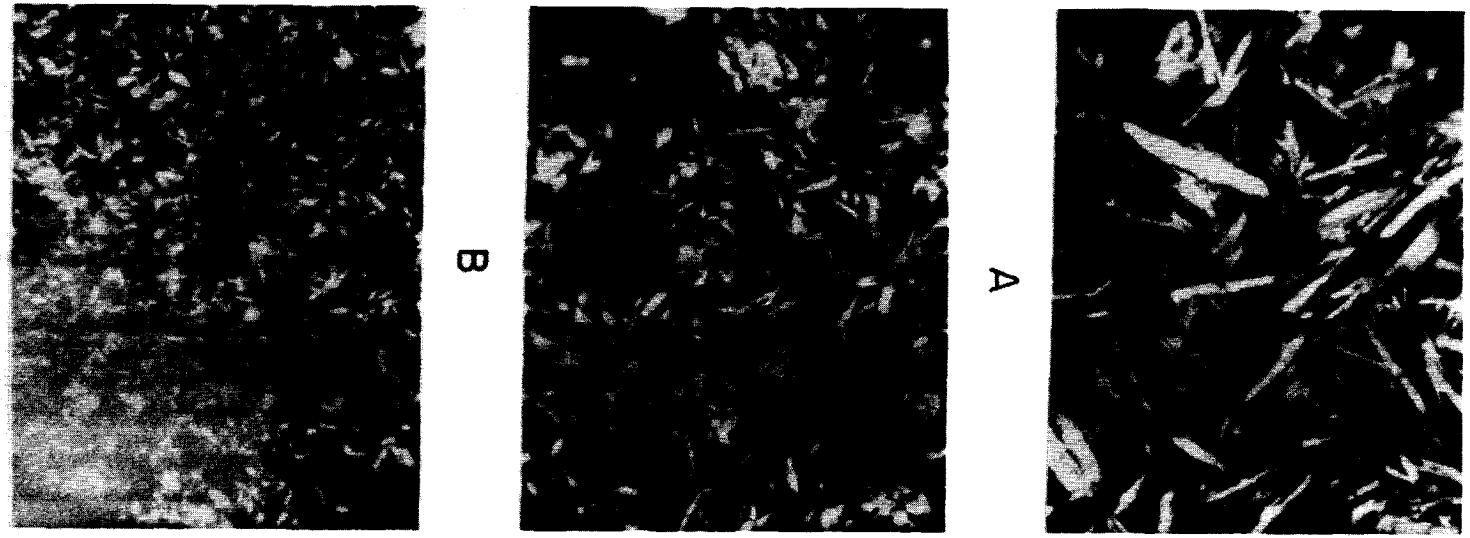

FIG. 7

EFFECT OF IODINE VALUE ON CRYSTAL SIZE IN HYDROGENATED RAPESEED OIL. A - SAMPLE S82; B - SAMPLE S75; C - SAMPLE S68.

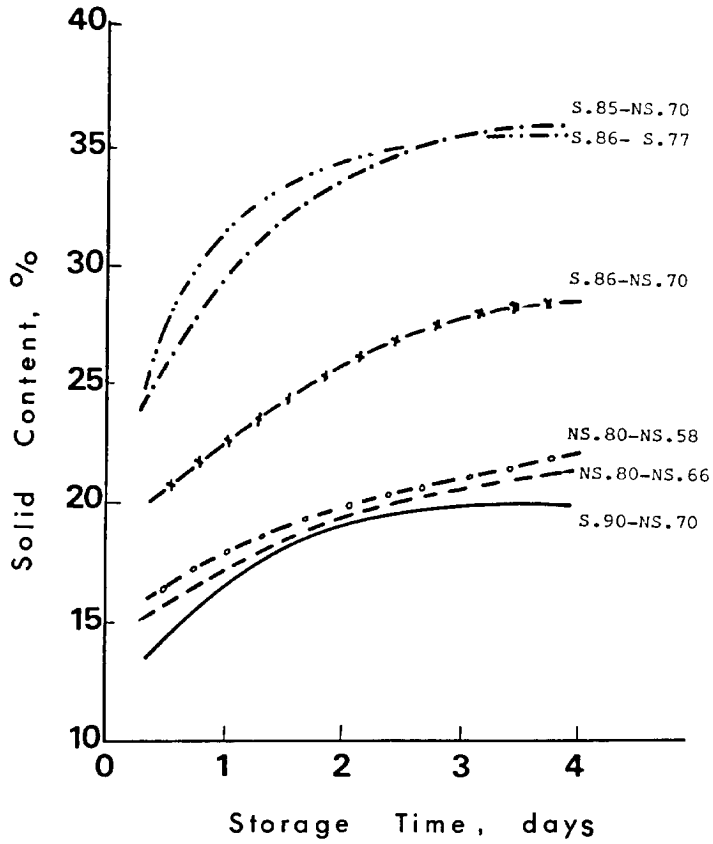

FIG. 8

SOLID FAT CONTENT OF HYDROGENATED RAPESEED OIL BLENDS AS A FUNCTION OF STORAGE TIME

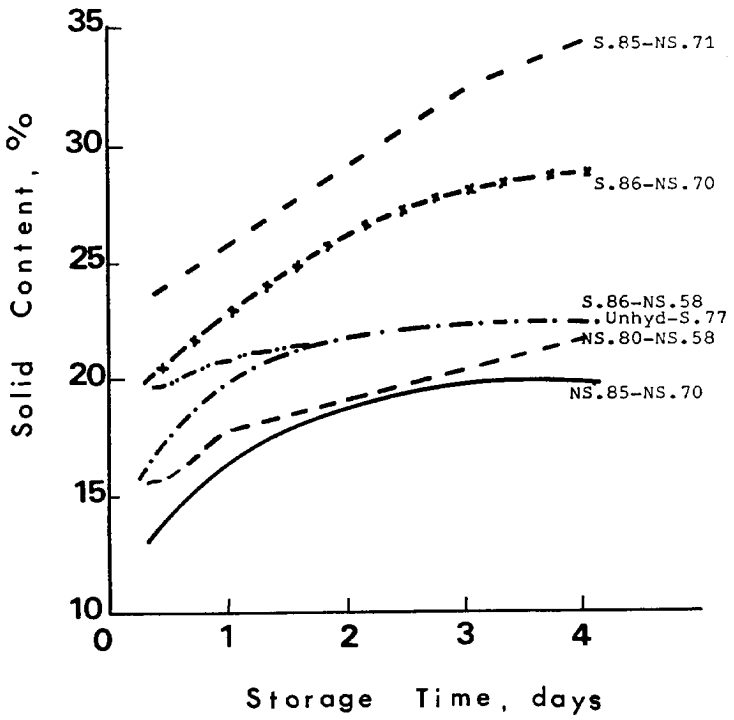

FIG. 9

SOLID FAT CONTENT OF HYDROGENATED RAPESEED OIL BLENDS AS A FUNCTION OF STORAGE TIME

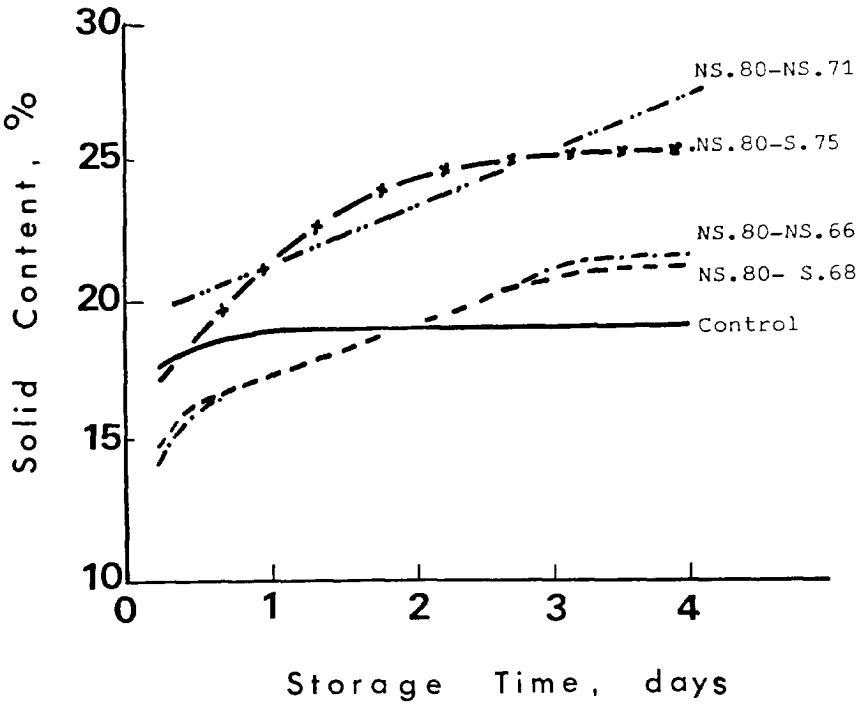

FIG. 10

SOLID FAT CONTENT OF HYDROGENATED RAPESEED OIL BLENDS AND CONTROL OIL AS A FUNCTION OF STORAGE TIME

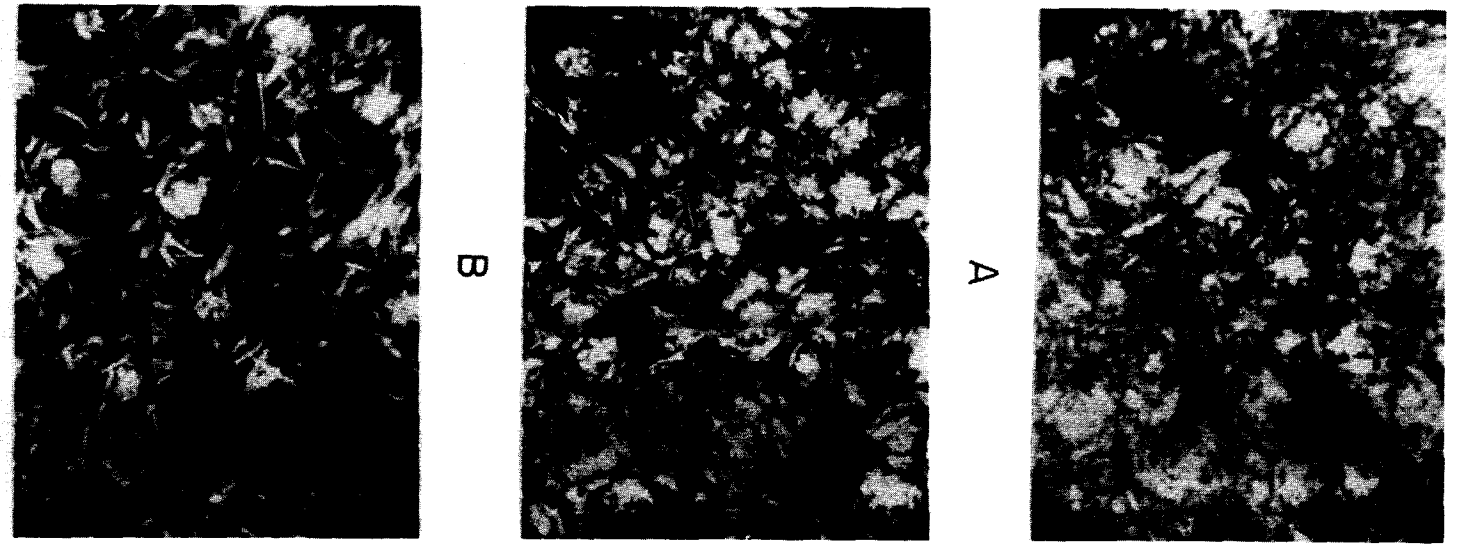

FIG. 11

CRYSTAL STRUCTURE OF MARGARINE BLENDS AFTER HOLDING AT 20°C. A - BLEND NS80 - NS58; B - BLEND S85 - NS70; C - BLEND S86 - S77.

FIG. 12

CRYSTAL STRUCTURE OF MARGARINES STORED AT 20°C.
A - BLEND NS80 - NS58; B - BLEND NS77 - S82;
C - BLEND S85 - NS71; D - S85 - S68;
E - S86 - S77.

FIG. 13

CRYSTAL STRUCTURE OF MARGARINES STORED ALTERNATELY AT 5°C AND 20°C. A - BLEND NS80 - NS58; B - BLEND NS77 - S82; C - BLEND S85 - NS71; D - S85 - S68; E - S86 - S77.

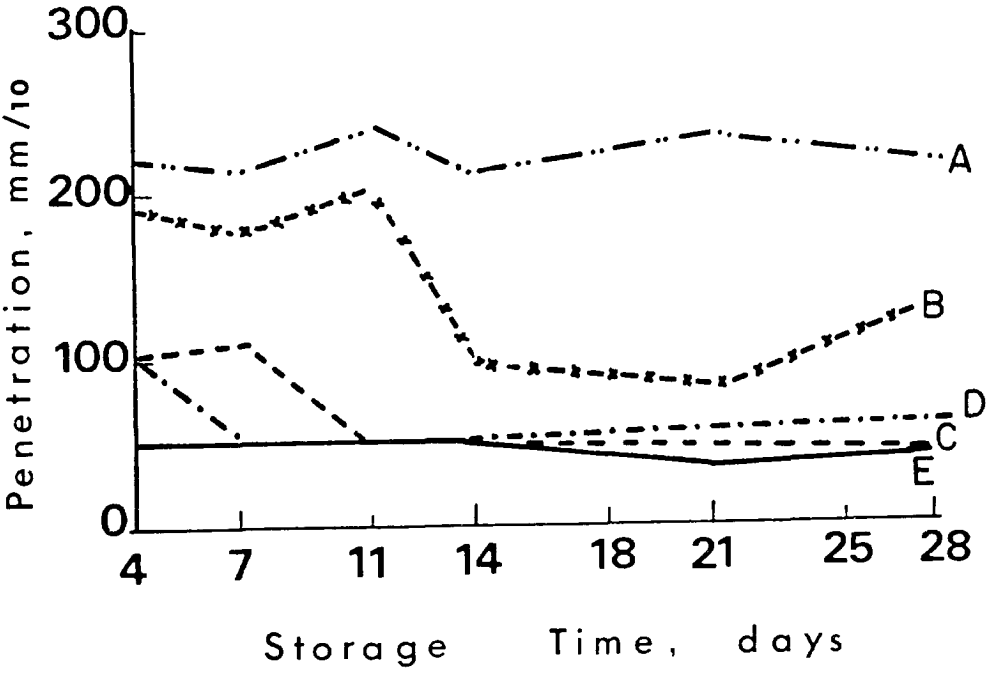

FIG. 14

CHANGE IN PENETRATION HARDNESS OF MARGARINES STORED AT 20°C. A - BLEND N580 - N598; B - BLEND N577 - 582; C - BLEND 585 - N571; D - 585 - 568; E - 586 - 577.

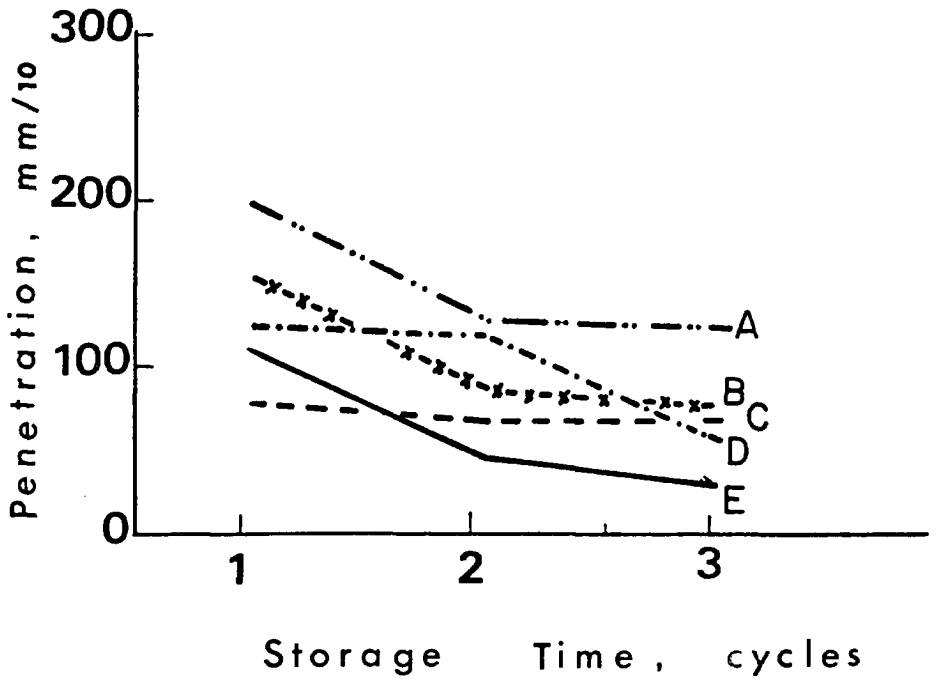

FIG. 15

CHANGE IN PENETRATION HARDNESS OF MARGARINES STORED ALTERNATELY AT 5° AND 20°C. A - BLEND NS80 - NS58; B - BLEND NS77 - S82; C - BLEND S85 - NS71; D - S85 - S68; E - S86 - S77.